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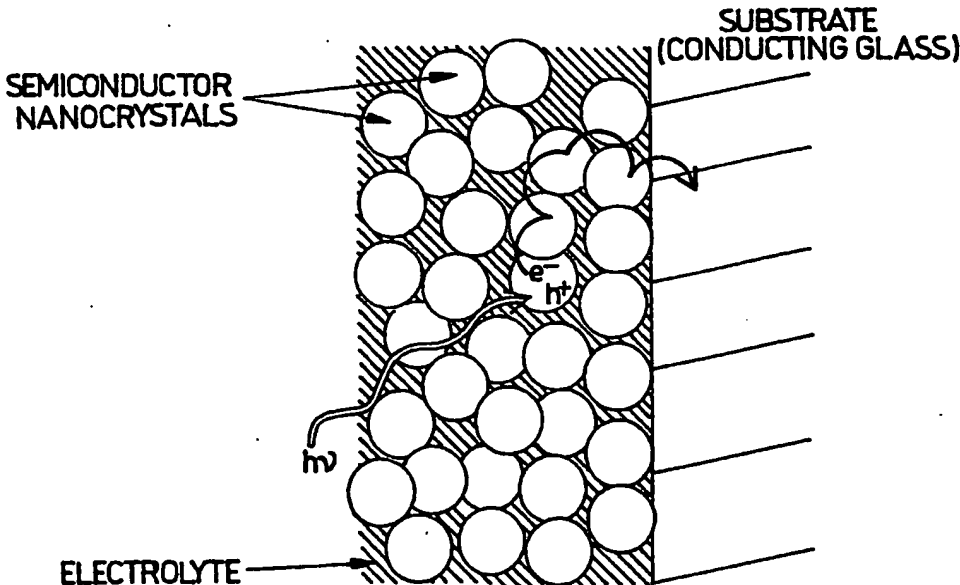
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: <b>PHOTOELECTROCHEMICAL CELL INCLUDING NANOCRYSTALLINE SEMICONDUCTOR LAYER</b>		
		
<p>(57) Abstract</p> <p>A cell, such as a photovoltaic cell, which includes a conductive substrate and a nanocrystalline semiconductor layer located on one side of the substrate. The semiconductor layer is of a thickness which is calculated, based on the nature of the impinging light, to minimize recombination losses.</p>		

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**Photoelectrochemical Cell Including Nanocrystalline Semiconductor Layer****FIELD AND BACKGROUND OF THE INVENTION**

The present invention relates to a photovoltaic or photochemical cell and, more particularly, to a photovoltaic or photochemical cell made of up  
5 of nanocrystals.

All photovoltaic (PV) cells depend on two principles for their operation. First, the creation of charges ( $e^-/h^+$  formation) by photon absorption. Next, the separation in space by a built-in electric field (the space charge layer). The first step requires only a semiconductor with a  
10 suitable bandgap. The second step requires a built-in electric field in the semiconductor. This is formed by generation of a junction which may be produced in various ways as follows.

One way applies for a p-n junction cell which is used in most types of photovoltaic cells. Here, either the surface is doped to make it the  
15 opposite conductivity type of the bulk semiconductor (e.g., p-n Si cells) or a layer of opposite conductivity type, and usually a different semiconductor, is deposited onto the first semiconductor forming a heterojunction cell, such as CdS/CdTe.

Another way involves the deposition of a metal onto a  
20 semiconductor of one conductivity type. A careful choice of both metal and deposition method is needed in these Schottky cells.

A third way calls for the immersion of the semiconductor in an electrolyte, which is usually a liquid but may be a solid, forming a

photoelectrochemical cell (PEC). A liquid electrolyte has the advantages of ease of formation and good contact between electrolyte and semiconductor, but has potential problems in terms of stability and sealing.

Electron/hole recombination in the space charge region is the cause  
5 for loss of quantum efficiency, and can occur by bulk and surface recombination. The latter is particularly important for polycrystalline semiconductors where the number of grain boundaries in the direction of charge transport is inversely proportional to crystal size. For this reason, polycrystalline films are sought with crystallite size as large as possible,  
10 usually greater than 1 micron.

Semiconductor films having small crystal size are much easier and cheaper to produce since, for example, they eliminate the high costs involved with using energy-consuming high temperatures. However, they normally exhibit prohibitively large recombination losses in photovoltaic  
15 cells. Small crystal size and low recombination losses are normally considered to be mutually exclusive properties.

Photochemical reactions on semiconductor colloids do show high quantum efficiencies in many cases, and here the small size is an advantage, since bulk recombination is negligible. See J. Moser and M.  
20 Gratzel, *Helv. Chim. Acta*, 65, 1436 (1982), which is incorporated by reference as if fully set forth herein. However, each colloidal crystal behaves as a complete 'cell' with both oxidizing and reducing reactions

occurring on the same crystal. They cannot be used to produce electricity as in a regular PEC, except in the case of slurry electrodes for semiconductor suspensions which exhibit low quantum efficiencies since, according to the mechanism postulated for these systems, the charged  
5 crystallites must make electrical contact with a collection grid before recombination occurs. See W. W. Dunn, Y. Kikawa and A. J. Bard, J. Am. Chem. Soc., 103, 3456 (1981), which is incorporated by reference as if fully set forth herein. Also, semiconductor colloids used for photochemical reactions are normally dispersed as a dilute phase in a  
10 liquid.

#### SUMMARY OF THE INVENTION

According to the present invention there is provided a cell, comprising: a substrate and a nanocrystalline semiconductor layer located  
15 on one or both sides of said substrate, said layer having thickness calculated to minimize recombination losses.

According to further features in preferred embodiments of the invention described below, especially where the device is used for the conversion of light into electricity, the conductive substrate is conductive.  
20 The substrate may be made of many suitable materials, such as conductive glass, and the like.

According to still further features in the described preferred

embodiments, the semiconductor layer is porous and has a thickness of from about 100 nm to about 1000 nm and, preferably, from about 200 nm to about 500 nm. The nanocrystalline semiconductor layer is made of crystals of average size of from about 3 to about 100 nm, preferably from about 4 to about 30 nm, most preferably from about 5 to about 20 nm.

According to another embodiment the cell also includes a second nanocrystalline semiconductor layer located on the other side of the substrate.

One embodiment of a device according to the present invention successfully addresses the shortcomings of the presently known configurations by providing a nanocrystalline photovoltaic cell which features significantly lower recombination losses than has been heretofore possible.

#### BRIEF DESCRIPTION OF THE DRAWINGS

15 The invention is herein described, by way of example only, with reference to the accompanying drawings, wherein:

FIG. 1 is a photoresponse curve (normalized so that each spectrum gives approximately the same peak response) as a function of wavelength for a PEC using a front-wall illuminated, chemically deposited CdSe film grown at 30°C on conducting glass under illumination from a quartz-iodine lamp (approximately equivalent to AM2 illumination) on conducting glass

20

for difference thicknesses of CdSe;

FIG. 2 is as described with regards to Figure 1 but for back-wall illumination;

FIG. 3 shows the I-V characteristics under solar illumination (920  
5 W/m<sup>2</sup>) of a 0.9 cm<sup>2</sup> CdSe film (deposited on both sides of double-sided  
conducting glass at 30°C under illumination during deposition; the total  
thickness of CdSe is about 120 nm) in a liquid junction photovoltaic cell  
configuration using an electrolyte of 1 M Na<sub>2</sub>S and 0.1 M S in water. The  
solid line indicates the illuminated I-V plot; the broken line indicates the  
10 dark I-V; the inset shows the transmission spectrum of the film;

FIG. 4 is a schematic model of a porous nanocrystalline film  
showing electrolyte contact with individual crystallites; illumination is  
shown to produce an electron/hole pair in one crystallite; the hole transfers  
to the electrolyte and the electron is shown traversing several crystallites  
15 before reaching the substrate;

FIG. 5 is a plot showing the absorption of blue and red light by a  
thin film in both front-wall (FW) and back-wall (BW) modes; the use of  
blue and red light were selected to illustrate long and short wavelength  
light, respectively;

20 FIG. 6 is as in Figure 5 but using a relatively thick film.



## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is of a photovoltaic or photochemical cell which uses a semiconductor film made up of nanocrystals and yet exhibits low recombination losses. Throughout, the term 'cell' is used to indicate  
5 a device for converting light energy into either electrical or chemical energy, or which uses light energy to catalyze a chemical reaction.

Porous nanocrystalline semiconductor films of CdS and CdSe can be used as photoelectrodes in photovoltaic cells with relatively low recombination losses. Spectral response measurements have been used to  
10 show how the recombination losses depend on film thickness. These nanocrystalline photovoltaic cells are shown to operate due to charge separation at the semiconductor-electrolyte interface rather than by a built-in space charge layer as normally occurs in photovoltaic or photoelectrochemical cells. The rapid removal of one charge by the  
15 electrolyte explains the low recombination loss.

The electrolyte used may be either liquid or solid. When the electrolyte is solid, the electrolyte is preferably applied to the nanocrystalline layer as a liquid, which subsequently solidifies. An example of this would be the use of polymer electrolytes which are formed  
20 from liquid precursors and subsequently polymerized. See M. Morita, T. Fukumasa, M. Motoda, W. Tsutsumi, Y. Matsuda, T. Takahashi and H. Ashitaka, J. Electrochem. Soc., 137, 3401 (1990), and references cited

therein, which is incorporated by reference as if fully set forth herein.

The principles underlying a cell according to the present invention can be better understood with reference to the accompanying Figures.

Without in any way limiting the scope of the present invention, the  
5 mechanism which gives the photovoltaic cells according to the present invention their unique and desirable characteristics, and the manifestation of the mechanism in measurable phenomena, are discussed below, after an example of the preparation of illustrative photovoltaic cells according to the present invention.

10 It is to be noted that in all photovoltaic cells light is absorbed in the semiconductor. This is technologically distinct from photogalvanic cells wherein light is absorbed by a sensitizer which then transfers charge to a semiconductor. Recent advances in the latter technology have been made whereby the underlying semiconductor layer is highly porous. The porous  
15 semiconductor layers described in N. Vlachopoulos, P. Liska, J. Augustynski and M. Gratzel, J.A.C.S., 110, 1216 (1988), which is incorporated by reference as if fully set forth herein, may be used as substrate in the devices according to the present invention.

The semiconductor films described here may be used also for  
20 photochemical cells, where a chemical reaction is driven or catalyzed by light. In such cells, the substrate need not be electrically conducting and may even advantageously be porous, allowing flow of solution through the

substrate. As for the photovoltaic cells described herein, the nanocrystallinity of the semiconductor deposited on, or distributed through, the substrate is of critical importance to the present invention.

According to the present invention, porous, nanocrystalline  
5 semiconductor films can be used as photoelectrodes with relatively low recombination losses, in spite of the nanocrystalline structure, i.e., crystal size on the order of 6 nm. Spectral response measurements show that above a certain layer thickness, which depends on crystallite size, recombination increases, and this increase depends strongly on the direction  
10 of illumination, whether it is front-wall or back-wall.

Charge separation in these photoelectrodes takes place at the semiconductor-electrolyte interface which are found throughout the thickness of the porous film, rather than by a built-in space charge field. The relatively low recombination losses are due to the rapid removal of  
15 one of the charges or holes allowing electrons to pass through a number of grain boundaries with a small chance of meeting a hole on its journey to the substrate. In some cases, the films show 'p-type' photoresponse behavior as would be expected if the direction of current flow were determined by the semiconductor surface/electrolyte boundary rather than  
20 by a field in the bulk of the semiconductor.

EXAMPLES

A film according to the present invention was prepared by electrodepositing CdS according to the method of Baranski et al. (A.S. Baranski, W.R. Fawcett, A.C. McDonald, R.M. de Nobriga and J.R. McDonald, J. Electrochem. Soc. 128, 963 (1981)), which is incorporated by reference as if fully set forth herein, from a DMSO solution of CdCl<sub>2</sub> (0.05 M) and S (0.1 M) under a constant current density of 1 mA cm<sup>-2</sup> onto a Ti substrate at 120°C. The CdSe film electrode was immersed in an aqueous solution of 1 M each KOH, Na<sub>2</sub>S and S. A second electrode of Pt was  
5 immersed in the same solution. When illuminated with tungsten-halogen light of 100 mW/cm<sup>2</sup> intensity, the photovoltage between the two electrodes was measured to be 0.26 V and the short circuit photocurrent was 0.19 mA/cm<sup>2</sup>.  
10

In another example, CdSe was chemically deposited onto SnO<sub>2</sub> coated glass (<10Ω) from an aqueous solution containing 80 mM CdSO<sub>4</sub>,  
15 nitriloacetate (KNTA) and 80 mM sodium selenosulphate. The Cd/NTA complex solution was adjusted to a pH of 9.5 (±1.5) with KOH solution. This solution and the Na<sub>2</sub>SO<sub>3</sub> solution (made by dissolving 0.2 M black Se in 0.4 M Na<sub>2</sub>SO<sub>3</sub> for several hours at about 60°C) were brought to the  
20 desired temperature and then mixed.

The substrates were put into the solution, which was then placed in a thermostatic bath under illumination from an ELH lamp roughly

equivalent to sunlight (AM2). Deposition occurred over several hours and the film was removed from the bath when a total thickness of 120 nm (60 nm per side) was reached. The film was made into a liquid junction photovoltaic cell as in the first example, but using an electrolyte 1 M in Na<sub>2</sub>S and 0.1 M in S. When illuminated in sunlight (920 W/m<sup>2</sup>), an open circuit voltage of 0.47 V and a short circuit current of 1.45 mA/cm<sup>2</sup> was generated.

To understand the results described above, it is convenient to start with the model of the junction between the nanocrystalline semiconductor layer and the electrolyte junction described previously, as shown in Figure

4. A photon is absorbed by one nanocrystal, forming an electron/hole pair. Since the direction of photocurrent flow is, in most cases, that of an n-type semiconductor, this means that the hole goes into solution where it oxidizes an electron donor, while the electron reaches the back contact, typically a conducting glass. Clearly, the farther the electron/hole pair is generated from the back contact, the greater the chance of the pair being lost by recombination.

This visualization of the phenomenon lends itself to the creating of a model which can be made for photocurrent generation as a function of average distance of charge generation from the back contact. An illustration of the model is shown schematically in Figures 5 and 6.

Figure 5 illustrates a thin film of CdSe, where a thin film is taken to mean a film of a thickness approximately equal to the absorption coefficient ( $\alpha$ ) for blue light.

For a thin film of CdSe (Figure 5), FW illumination with blue light leads to absorption of most of the light relatively close to the substrate because the film is thin. For red light, the situation is similar except that the absorption of the light is not as strong. No appreciable difference is expected for BW illumination, as is evident from Figure 5.

For a thick film, defined as one which is considerably larger than  $\alpha$  for blue light, FW illumination with blue light results in most of the charge carriers being generated relatively far from the substrate, and the electrons being as a result more susceptible to recombination loss. With FW red light illumination, more carriers are generated closer to the substrate. This should lead to a poor photocurrent response for short wavelength light, which improves with increase in wavelength until the band edge is reached, at which point the response drops again. Also, the long wavelength response should improve with increasing thickness (up to a certain point) since more of the long wavelength light is absorbed.

Considering now BW illumination of the thick film, the situation is reversed compared with FW illumination. In the case of BW illumination, blue light is absorbed close to the substrate while red light is absorbed further away. This should result in a good response for blue light, with the

close to bandgap response poorer than for FW illumination, since some of this light is absorbed relatively far from the substrate.

CdSe films deposited on conducting transparent glass were used, thus allowing illumination from either side of the film, i.e., either front-wall [FW] or back-wall [BW] illumination.

Crystallite sizes can be measured by electron microscopy or estimated from the transmission spectra. Using the latter method, it is estimated that the crystal sizes for the samples used in Figures 1 and 2 are about 6.5 nm.

10 The results described above demonstrate that in order to obtain optimum photocurrents from photovoltaic cells based on these nanocrystalline films, the optimum configuration will often be a thin film deposited on both sides of double sided conducting glass. Figure 3 shows I-V characteristics, both dark and illuminated, of such a CdSe bi-film with  
15 the transmission spectrum of the film shown in the inset.

It is to be noted that attempts to make a solid state Schottky junction with these films resulted in a high resistance I-V characteristic, which was virtually collinear with the voltage axis, and little, if any, photoeffect, as described in Hodes et al.

20 Two methods were employed to control crystal size in these films. One way was by controlling the deposition temperature. Another involved the use of illumination during deposition. An increase in either the

deposition temperature or the illumination during deposition led to an effective increase in crystal size.

When illumination was used during deposition, the spectral responses shown in Figures 1 and 2 were obtained. Quantum efficiency measurements for these films in the region of strong absorption and flat photocurrent response gave values typically between 0.6 and 0.7.

The behavior to be expected based on the above model corresponds closely to the results in Figures 1 and 2 in all aspects, which attests to the accuracy of the model. In addition, the thickness at which the peak in the spectra first begins to appear gives an indication of the thickness of the active layer of CdSe. For thicknesses greater than this thickness, light absorbed in the region farthest from the substrate (blue for FW and red for BW illumination) will be subject to increasing recombination and resistance losses. For the films with crystal size of about 5.0 nm, this thickness is about 150 nm, while for the film in Figures 1 and 2 (crystal size of about 6.5 nm), it is about 300 nm.

While these thicknesses may seem thin if close to total absorption of light is desired, as would be the case for solar cell use, it should be noted that the oscillator strength, and therefore the absorption coefficient of these size-quantized films may be enhanced relative to bulk material.

The  $\alpha$  in the region of strong absorption is about  $2 \times 10^5 \text{ cm}^{-1}$  for the approximately 5.0 nm crystallites and about  $1 \times 10^5 \text{ cm}^{-1}$  for the 6.5 nm



crystallites. This is to be compared with approximately  $1 \times 10^5 \text{ cm}^{-1}$  for 'normal' CdSe. Hence, preferable film thicknesses for maximum absorption would be range from approximately two or approximately three times those thicknesses at which peak behavior for FW illumination start to be exhibited. Glass with a conducting layer on both sides, and with the semiconductor deposited on both sides, would come close to fulfilling this requirement.

There are two loss mechanisms in films such as those described herein as the thickness increases. First, there is a resistance loss, leading to loss in photovoltage and fill factor. Second, there is a recombination loss, presumably occurring at crystal boundaries, which leads to loss in photocurrent. These losses are in addition to the possibility of indirect recombination by electron injection into the electrolyte, which is probably the predominant loss mechanism for thin films. These recombination losses amount to 30-40% reduction in efficiency, as described earlier.

Direct recombination is relatively low for LJ's in contrast to a solid junction because the holes are removed rapidly by the electrolyte, which lowers the recombination probability.

The mechanism for charge separation described herein is quite different from that in a conventional PEC or PV cell. In effect, these films behave as colloidal semiconductors. It is generally accepted that the existence of an appreciable space charge layer in small lightly doped

semiconductor particles is unlikely, since the particle is too small to support a field in its bulk. See A. J. Bard, J. Phys. Chem., 86, 172 (1982), which is incorporated by reference as if fully set forth herein.

In such a case charge separation occurs at the particle surface by  
5 transfer into the electrolyte. For a colloidal system, such a charge transfer is measured by the degree of chemical reaction occurring due to either or both hole and electron transfer. The two reactions are different, resulting in a non-regenerative system. If the reduction and oxidation reactions were the same, forming a regenerative system, no net change, other than heat  
10 production, would occur.

For the films described here, however, both regenerative and non-regenerative reactions can be used, and in the former case, the system acts as a PV cell with electricity being produced. However, in contrast to other PV systems, and in common with dispersed colloidal photochemical  
15 systems, charge separation occurs not by a space charge layer, but rather by differing rates of electron and hole transfer into solution.

It will be clear that the methods used to prepare films according to the present invention may include most of the methods commonly used to deposit semiconductor films, and, in addition, some less commonly used  
20 methods. Because it is desired to produce crystals of small size, in contrast with the large crystal size normally required for photovoltaic cells, the preparation techniques can be based on low temperature techniques, using

temperatures on the order of 0 to 200°C, rather than on the more common but more demanding higher temperature techniques taking place at temperatures of 400 to 600°C. Use of low temperature techniques dramatically the energy consumption and thus the cost of manufacture.

5        Besides the methods of electrochemical deposition and chemical solution deposition described in the examples above, vacuum evaporation and sputtering (vacuum deposition) onto substrates which are at approximately room temperature or even cooler will give small crystal size. The presence of an inert gas under low pressure during vacuum  
10 evaporation will help to form the small crystal sizes required. However, a large variety of low temperature methods, including, but not limited to, electrophoresis, anodization, and those mentioned above, can effectively be used. Another fabrication technique involves the successive immersion of the substrate in solution of the ions making up the semiconductor.

15        The porosity of the film may be controlled by depositing a composite of the desired semiconductor together with an easily dissolvable material. This may be desirable to increase the rate of diffusion of solution species in the porous film. Thus, as example, CdSe could be evaporated or sputtered together with Al (from separate sources) and the Al  
20 subsequently dissolved by an alkali metal hydroxide solution (which will not dissolve the CdSe). As long as the concentration of Al is not too high (in which case the film would disintegrate) this will trace a film of porosity

depending on the ratio of CdSe to Al.

For porous substrates (which, for photochemical reactions, may be either conductive or non-conductive and preferably transparent to the illumination), simple successive immersions of the substrate in solutions of the ions making up the semiconductor may be sufficient. For example, to prepare CdS on a porous substrate, the substrate may be dipped first in a solution of a cadmium salt, then in a sulfide solution (or vice versa).

While the focus throughout the above description has been on use of devices according to the present invention as photovoltaic cells for the production of electrical power, it will be clear that nanocrystalline semiconductor layers according to the present invention may also be used for both photocatalytic and photoconversion reactions, when the system is non-regenerative.

Thus, instead of the production of electricity being the primary product, chemical energy, in the form of desired chemical products, becomes the primary product. While ostensibly a radical departure from use of devices according to the present invention as solar cells, it should be appreciated that the only difference is that, in the case of electricity production, the electrolyte is chosen so that whatever is oxidized (reduced) at the semiconductor electrode is reduced (oxidized) back to the original reactants at the second electrode, while in the case of chemical production, the electrolyte is so chosen that the reactions at the two electrodes are

different and there is a net production of new chemical products.

An example of this is the photoelectrolysis of water. If dissolved oxygen is present at the non-semiconductor electrode, the oxygen is reduced to water, exactly balancing out the evolution of oxygen at the n-  
5 type semiconductor electrode. In this case the only net production is of electrons. However, if oxygen is absent, hydrogen may be evolved instead, making the device a chemical cell.

An example of a photocatalytic reaction where such films may be of used is the photo-oxidation of small amounts of organochlorine or  
10 cyanide contaminants in water. See C. Korman, D. W. Bahnemann and M. R. Hoffman, Environmental Sci. & Tech., 25, 494 (1991), which is incorporated by reference as if fully set forth herein.

The advantage of the porous layers over more usually proposed suspensions or colloids of the semiconductor is that the semiconductor is  
15 present in a convenient, immobilized form on a substrate which can be easily immersed and removed from the water, unlike the case with the removal of a dispersed suspension.

For such purposes, the substrate itself may also be porous and of high surface area. A preferred embodiment in this case might be a flow-  
20 through 'membrane' whereby the water to be purified flows through the illuminated porous semiconductor and porous substrate.

While the invention has been described with respect to a small number of preferred embodiments, it will be appreciated that many variations, modifications and other applications of the invention may be made.

## WHAT IS CLAIMED IS:

1. A cell, comprising:
  - (a) a substrate; and
  - (b) a nanocrystalline semiconductor layer located on one or both sides of said substrate, said layer having thickness calculated to minimize recombination losses.
2. A cell as in claim 1 wherein said substrate is conductive.
3. A cell as in claim 1 wherein said semiconductor layer is porous.
4. A cell as in claim 2 wherein said conductive substrate is conductive glass.
5. A cell as in claim 1 wherein said semiconductor layer is of a thickness of from about 100 nm to about 1000 nm.
6. A cell as in claim 1 wherein said semiconductor layer is of a thickness of from about 200 nm to about 500 nm.
7. A cell as in claim 1 wherein said nanocrystalline semiconductor layer is made of crystals of average size of from about 3 to about 100 nm.
8. A cell as in claim 1 wherein said nanocrystalline semiconductor layer is made of crystals of average size of from about 4 to about 30 nm.

8. A cell as in claim 1 wherein said nanocrystalline semiconductor layer is made of crystals of average size of from about 5 to about 20 nm.

10. A cell as in claim 1 further comprising a second nanocrystalline semiconductor layer located on the other side of said substrate.

11. A cell as in claim 1 further comprising an electrolyte in contact with said conductive substrate and said porous nanocrystalline semiconductor layer.

12. A cell as in claim 11 wherein said electrolyte is in the liquid form.

13. A cell as in claim 11 wherein said electrolyte is in the solid form.

14. A cell as in claim 13 wherein said electrolyte is applied in the liquid form and subsequently solidifies.

15. A cell as in any of claims 11-14 further comprising a second electrode in contact with said electrolyte.

16. A cell as in claim 1 wherein said semiconductor layer is fabricated by chemical solution deposition.

17. A cell as in claim 1 wherein said semiconductor layer is fabricated by electrochemical deposition.



18. A cell as in claim 1 wherein said semiconductor layer is fabricated by vacuum deposition.

19. A cell as in claim 1 wherein said semiconductor layer is fabricated by successive immersion of said substrate in solution of the ions making up said semiconductor.

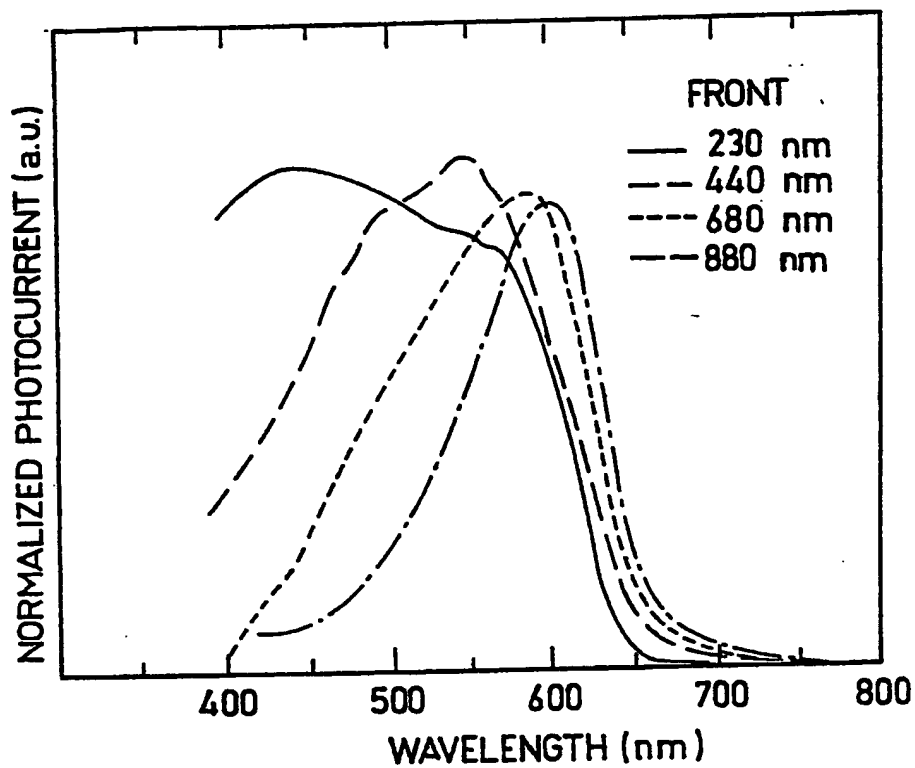


FIG.1

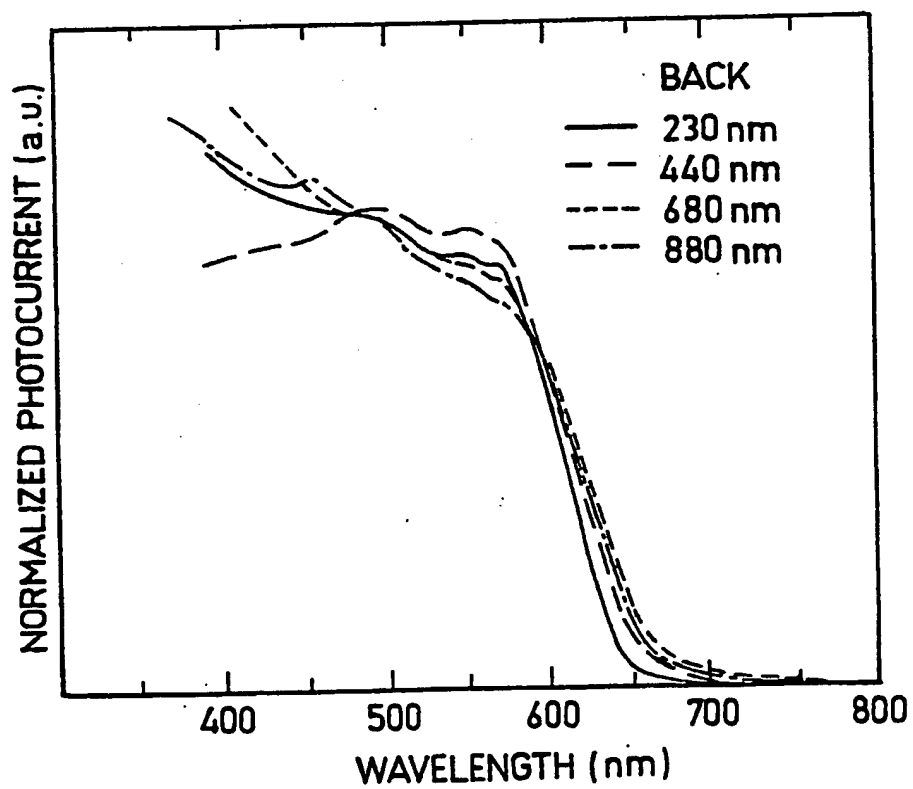


FIG.2

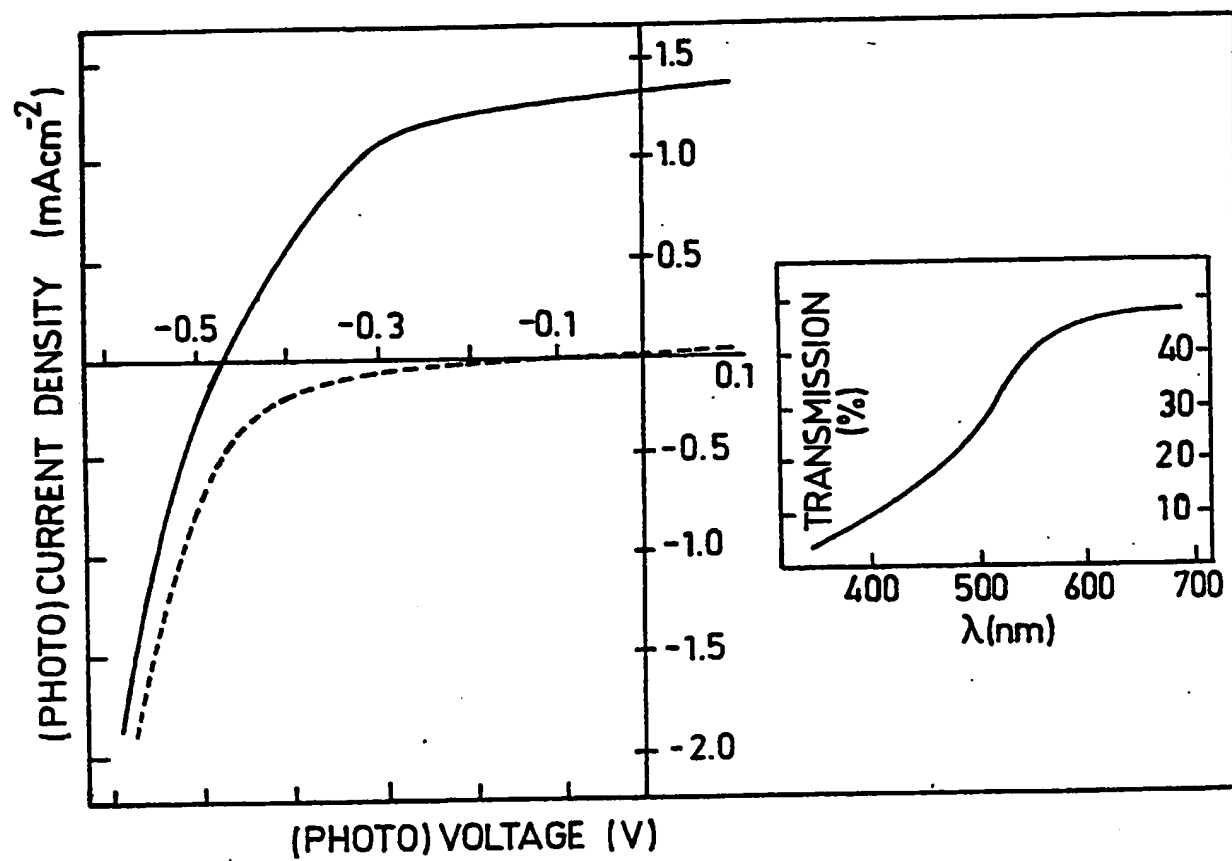
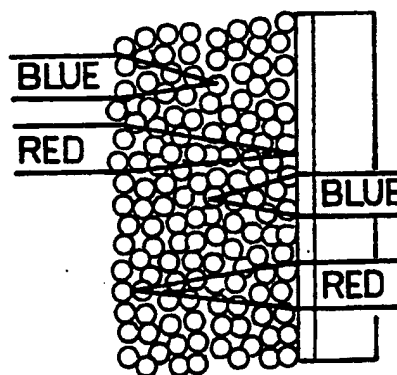
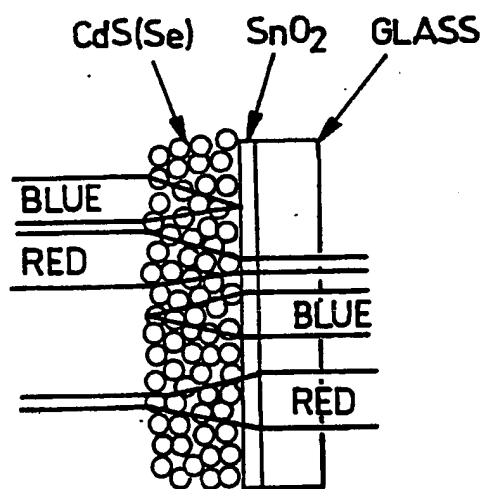
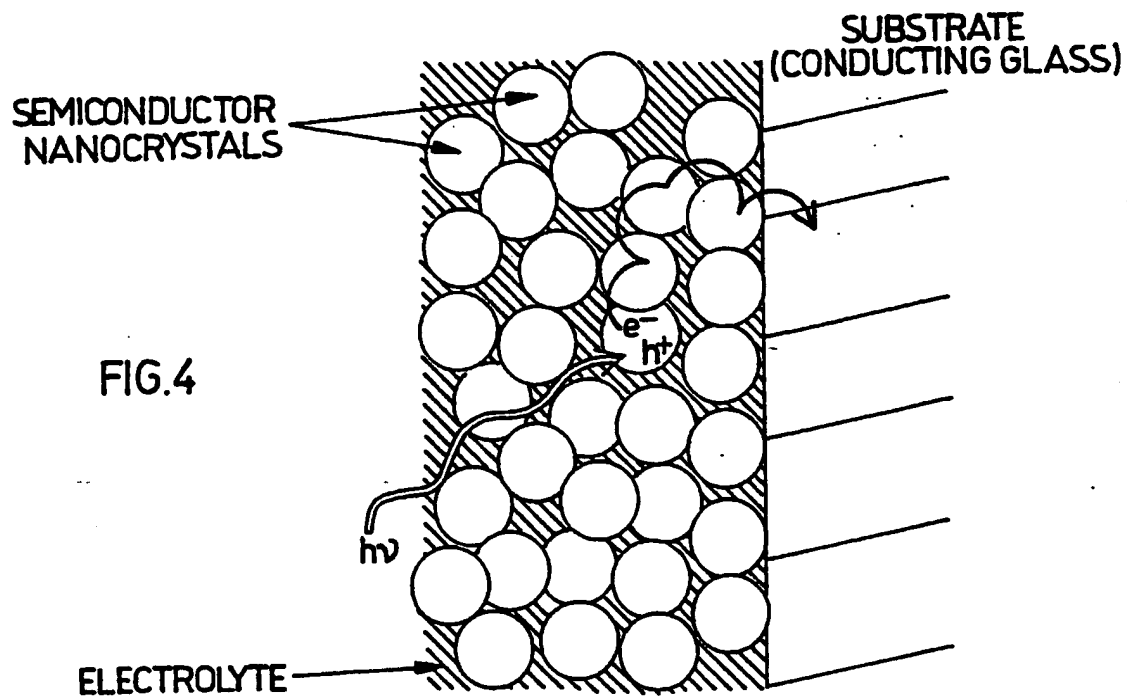


FIG.3



## INTERNATIONAL SEARCH REPORT

International application No.

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**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :IPC (5): H01M 6/36

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According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)...

U.S. : 136/260; 429/111

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US,A 4,544,470 (Hetrick) 01 October 1985 (See col. 3, line 61 Through Col. 4, line 38).	<u>1-3,5-8,11-12</u> 1-8,11-12
X Y	Electrochimica Acta, January 1987, Vol. 32, No. 1, E. Fatas et al., "Electrodeposition And Characterization of CdS Thin Films On Stainless Steel And Tine Oxide Substrates", pp. 139-148 (See Table 1, last column).	<u>1 - 9 , 11 -</u> <u>12,15,17</u> 1-9,11-12,15-19
Y	Journal of Power Sources, September 1988, Vol. 24, N. Khare, "A Cadmium Sulphide Solid Electrolyte Photoelectrochemical Solar Cell", pp 121-125 (see entire article).	13-14

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"A"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

22 SEPTEMBER 1993

Date of mailing of the international search report

- 0 OCT 1993

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/06141

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A 4,637,969 (Skotheim et al), 20 January 1987 (See Figure 1 and Col. 3, lines 4-59).	13-14